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(54) Title: COMPOSITION CONTAINING NBR AND THERMOPLASTIC ELASTOMER

(57) Abstract: The present invention relates to an NBR copolymer and thermoplastic elastomer composition. The invention further relates to a pre-crosslinked NBR copolymer and thermoplastic elastomer composition, in which the NBR is pre-crosslinked by addition to the composition of a crosslinking monomer having a functionality equal or higher than 3, said crosslinking monomer being selected from divinyl benzene, trimethylol propane trimethacrylate, ethylene glycol dimethacrylate and triallyl isocyanate. Said compositions are specially useful for shoes industry, toys, coils, gaskets and any other article made of rubber. Said rubber produced according to the present invention exhibits improved mechanical, chemical and dull look properties.

COMPOSITION CONTAINING NBR AND THERMOPLASTIC ELASTOMER

FIELD OF THE INVENTION

5 The present invention refers to NBR copolymer
thermoset elastomer compositions or mixtures, or NBR
copolymers with a crosslinking agent, with the thermoplastic
elastomers having improved surface and dullness or opacity
10 properties. Application of these mixtures can be found in
the shoes industry, that is, in shoe soles and similar,
tubes and hoses, toys, coifs, gaskets and any other article
made of rubber. The present invention also relates to
vulcanizable NBR and thermoplastic elastomer copolymer or
terpolymer mixtures or compositions.

15 BACKGROUND OF THE INVENTION

It is common knowledge that vulcanized rubber and
also thermoplastic rubber are used in shoe soles. However,
the use of thermoplastic polymers results in a rubber with a
brightness aesthetically not accepted by the shoe industry.
20 These mixtures are generally constituted of thermoplastic
elastomers such as SBR, SSBR, and so on with polybutadiene.
Due resulting brightness in the final product, this would
have to be further subjected to a dulling process to produce
an aesthetically useful article for shoe soles. Besides
25 brightness these rubbers have poor mechanical properties,
such as processability, strain, elasticity, abrasion and
elastomeric memory and other properties.

The elastomeric mixture technology is rapidly
improving, mainly in the case of elastomeric mixtures to
30 produce thermoplastic elastomers. All this shows that this
tendency, named technology tendency will grow in the polymer
industry. This means that less emphasis will be given to the
development of new materials derived from totally new
monomers. This means that from now on more improved

materials formed from mixtures and composite materials, from known polymers will be produced.

Due to a need for obtaining a rubber with vulcanized rubber characteristics, without the disadvantages of the groups of thermoplastic rubbers of the prior art, the present inventors have concentrated their aim at the structural morphology of elastomeric materials, in an attempt to control physical, chemical, rheological and surface properties of thermoplastic materials.

The main idea arised from the fact that most polymers, when mixed, wiold two phases inside their morphology, this being predominant in all thermoplastics, as they are structured by "soft domain" (polybutadiene) and "hard domain" (styrene).

The polymer found in greater concentration would be the continuous phase with the second polymer soaked between them thus, forming a discrete continuous matrix. In 1962, Drs. Walter and Klyte demonstrated in their studies that most mixtures form small "heterogeneous" zones, with an extension of approximately $0,5\mu\text{m}$. This extension zone is called "closing" or "pseudo - crosslinkage". Due to this physical - chemical phenomenon, certain elastomeric behaviours can be found in these "thermoplastic" materials. However it has been proved that some of these mixtures or "high performance polymers" consist of small phases in "discrete zones", as described before. These phases are within a continuous matrix with a larger phase. Another outstanding feature occurs during the "inversion" of phases, which occurs when these "thin plates" have an extension of approximately $0,5\mu\text{m}$ of the fraction of the molecular interpenetrations between them, which brings up unpleasant effects to their physical and mechanical properties, such as:

- a. high module;
- b. high thermoplastic strain

- c. low abrasion resistance
- d. low tearing resistance
- e. plastic appearance

These are undesirable characteristics in
5 thermoplastic elastomers for specific uses, as for example
in shoe products.

The new studies developed here have demonstrated
that large "inter - closing" zones depend, directly, on the
volume fraction and the intrinsic viscosity relation of the
10 used elastomers, that is, a main factor for the elastomeric
mixtures to show physical and mechanical acceptable
properties. All this depends on "inter facial linkage
extensions", which occur between the used elastomers, in
particular when they exhibit different reactivities, a
15 phenomena observed when thermoplastic elastomers or mixtures
undergo swelling tests (solvating), in which only a portion
of the elastomer swells, as the referred to elastomer
portion does not show "inter - closing" with the other
phase, due to the fact that is larger and continuous.

20 Recent works have emphatically shown the
obtainment of new mixtures for the thermoplastic elastomer
production. Thermoplastic elastomer mixtures are
characterised as materials, which can be processed when,
submitted to friction and temperatures and, later, when they
25 are cooled they show properties similar to the vulcanized
elastomers.

When most thermoplastic elastomers are compounded
or formulated, they must be assisted by additives such as:
mineral fillers, plasticizing oils, antioxidants and high
30 tenacity polymeric mixtures (high impact polystyrene), to
improve, as they say, their final properties, such as:
abrasion, tearing and stiffness with the circumstantial
reduction of their flow property, when using calcium
carbonate and silica, thus requiring the use of 5 to 30
35 parts of high impact polystyrene in the formulation. Then

the undesirable fact occurs. The discrete thermoplastic phase from the polystyrene with a lesser proportion in the diblocked elastomer (styrene butadiene) is increased in a disproportional way and the elastomeric phase of the polybutadiene is diminished. Addition of high impact polystyrene homopolymers, when aggregated to the diblocked polymers increase disproportionately the Yong modules, which normally, with the addition of plasticizing oils cause the reduction of these modules. Further it is worth to mention that the diblock SBS thermoplastics are very elastic during their softening in the process phase. This is due to the retention of the two phases and their "interclosed" structures above the glass transition temperature (T_g) of the blocked polystyrenes.

Other disadvantage found in the prior art was the plastic's characteristic brightness over the surface of the finished product, mainly in shoe soles, as well as elastomeric memory loss. To prevent these undesirable effects on those products one uses polybutadiene thermoplastic elastomers with high syndiotacticity or with crosslinkage, which reduce the modules making them lower, improves their elastomeric properties and render them dull. These features cannot be found in all thermoplastics, when high impact polystyrenes are used therein. Due to this apparent deficiency there is a demand in the shoe industry for lighter and more practical new materials, such as thermoplastics, which would be the ideal candidates for an excellent productivity and a minimal possible loss (vulcanized cuttings), increasing their versatility and diminishing the labor required for vulcanized elastomers. Thus, nowadays there is an incessant search for rubber articles in order to obtain the physical features described above, as well as the dullness in the final product.

To overcome those drawbacks of the prior art, the present inventors developed a rubber from a mixture of

thermoplastic with NBR or a pre - crosslinked NBR, in which addition of NBR or pre - crosslinked NBR (NBR + monomer + crosslinked agent) provide dull thermoplastic elastomers.

ABSTRACT OF THE INVENTION

5 The present invention consists of a thermoset NBR copolymer polymeric elastomer composition or a NBR copolymer plus a crosslinking agent, with thermoplastic elastomers, wherein they exhibit improved mechanical and surface properties, as well as a final dull product. The present
10 invention also refers to a vulcanizable polymeric composition.

DETAILED DESCRIPTION OF THE INVENTION

 The object of the present invention is to provide a polymeric composition, comprising from 5 to 95 parts of
15 NBR per 100 parts of the composition with thermoplastic elastomer.

 Another object of the invention is to provide a polymeric composition comprising from 5 to 95 parts of NBR terpolymer - crosslinking agent per 100 parts of the
20 composition with polymeric elastomer, in which the elastomer is selected from monoblocked, diblockerd, triblocked, radial or linear thermoplastic elastomers.

 Another object of the invention is to provide a vulcanizable polymeric composition comprising from 5 to 95
25 parts of (NBR) butadiene-acrylonitrile copolymer or a terpolymer of butadiene-acrylonitrile-butadiene (NBR)-crosslinking monomer per 100 parts of the composition with thermoplastic elastomer and an effective amount of a vulcanized system.

30 The crosslinking agent used in the composition is selected from monomers with a functionality equal or higher than 3. Preferably, the agents or crosslinking monomers are selected from divinyl benzene, trimethylol propane trimetacrylate, ethylene glycol dimetacrylate and triallyl
35 isocyanurate.

In general, by elastomeric material it is meant the one, which can be drawn to 100% of its original size, without losing its return, that is, it returns to its original size in a short period of time. This effect has
5 been observed in the compositions of the invention made from thermoplastic elastomers and NBR, with the difference that the modules diminish proportionally to the crosslinkage degree and to the amount of acrylonitrile used in the NBR copolymer, which does not occur in thermoplastic elastomers
10 without the presence of NBR.

Modified thermoplastic elastomers and thermoelastic mixtures exhibit strain/deformation features, this fact being proved in thermoplastic elastomers as they have low modules, typical of crosslinked elastomers (C
15 curve) and other high modules producing materials undergo from a high degree of plastic deformation (B curve).

GRAPH

tensão: strain

deformação: deformation

20

A) HIGH PLASTIC MODULE

B) HIGH MODULE WITH POOR CYCLE RETURN

C) LOW ELASTOMERIC MODULE

By using the polymeric mixtures, physical properties can be altered thus, producing materials, which
25 can be used in a great number of applications in several different industries.

Referring to the above mentioned, a profound study has led to polymer mixtures butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer
30 terpolymer and to vulcanizable polymeric mixtures, comprising butadiene-acrylonitrile copolymers or butadiene-acrylonitrile-crosslinking monomer terpolymer and a vulcanization system, which exhibit low module properties. The term "crosslinking monomer" includes conventionally
35 known monomers in the art as polymerizable crosslinking

agents, in combination with other traditional monomers. Typically, as mentioned above, these crosslinking monomers include monomers with a functionality equal or higher than 3, such as divinyl benzene, trimethylol propane trimethacrylate, ethylene glycol dimethacrylate and triallyl isocyanate, 1, 3 dimethacrylate butilene, allyl metacrylate, or any other crosslinking agent known from the art. In the present invention, the term "NBR copolymer or terpolymer of butadiene-acrylonitrile-crosslinking monomers agent" is simply called NBR. The polar acrylonitrile monomer content can vary from 1 to 60%, preferably from 5 to 50% and more preferably from 15 to 45% by weight based on the butadiene weight.; the crosslinking agent varies from 0 to 20%, preferably from 0 to 10% and more preferably from 0 to 5% by weight based on the weight of acrylonitrile and butadiene. These copolymers or terpolymers are capable of producing effects only presently found by using syndiotactic polybutadiene polymers when mixed with some blocked, diblocked, triblocked polymer thermoplastics (styrene - butadiene - styrene, (SBS), styrene - isoprene-butadiene-styrene (SSBS), styrene - isoprene - butadiene - styrene (SIBS), styrene- isoprene-styrene (SIS), independently if they are linear or radial in their basic structure. NBR in the polymeric composition presents an excellent compatibility in concentrations from 5 to 50 parts, preferably from 5 to 40 parts, more preferably from 5 to 30 parts, and much more preferably from 5 to 20 parts per 100 parts of elastomer, exhibiting superior or equal physical and mechanical characteristics in different used proportions when compared with syndiotactic polybutadiene conventionally used in thermoplastic elastomer compositions, so as to produce the desired effects in the shoe industry, mainly when partially crosslinked NBR copolymers with shrinkage values between 0 and 15%, 0 and 20%, 0 and 30% or 0 and 40% are used. It has been clearly observed that these long

branched chains were inter - closed with the base polymer providing an intermolecular linkage and thus forming a web between the thermoplastic elastomer discrete phases and the NBR copolymers. The thermoplastic elastomer final mixtures
5 with varied NBRs present mechanical properties on the same level or superior to those produced by thermoplastic elastomers and syndiotactic polybutadiene. Syndiotactic polybutadiene is world-wide produced only by "Japan Synthetic Rubber Co.", and nowadays this company cannot
10 supply the worldly demands. Customers from all over the world purchase such products under share regime, due to the fact that annual production of syndiotactic polybutadiene is not capable of attending the world requirements. It is also an object of the present invention to offer to the market an
15 alternative to the shortage of this product, also providing the development of new applications of thermoplastic rubbers not so much explored until now.

The intermolecular linkages between thermoplastic elastomer matrix in combination with the intermolecular
20 linkages of the butadiene-acrylonitrile-crosslinking monomer terpolymer, generate a crosslinked structure in three dimensions, which upon melting during the moulding step returns to its original position after melting. In this return the intermolecular linkages and the intramolecular
25 linkages play fundamental role either in maintaining a good level of mechanical properties or in the dullness showed by the mixture. Crosslinkages withstand the melting process without tearing. Thus, after their post-melting cooling, these crosslinkages maintain the interclosed structures of
30 the mixture stiffening the polymeric structure, now cold, thus producing a microscopic wrinkling on the artifact surface. This multifaceted surface on a microscopic level is responsible for the chaotically incident light refraction, exhausting the artifact brightness, so as to give it the
35 final dull appearance.

If there is not such a type of "anchoring" or "fastening" of chains, after their relaxing in the melting step, there is no sufficient elastic memory to pull these chains and create a superficial microwrinkling, responsible for the final dull appearance of the artifacts, after moulding.

The NBR /thermoplastic elastomer compositions of the present invention, as they have allyl carbons in both compounding basic polymers, in relation to the mere coming from butadiene, can also be submitted to the same conventional process steps as the non thermoplastic elastomers are submitted, i.e., they can be vulcanized with systems based on sulphur or its donors or with peroxide based systems, with or without the use of co-agents, then resulting in the polymeric composition mentioned before. Further, the present compositions can be moulded by conventional rubber industry processes.

Vulcanization system is selected from the following products conventionally utilised in the vulcanized rubber manufactures, such as: sulphur and/or its donors, primary accelerators, secondary accelerators, tertiary accelerators, peroxides, sylanes, crosslinking agents and their mixtures and electron accelerators.

In the present specification, the expression "efficient amount of vulcanizing system" means the amount routinely used in the field of vulcanized rubber manufacture. This amount will depend on the vulcanizing system used and also on the origin of the products employed in the vulcanizing system. These amounts are only given for illustrative purposes.

Sulphur based vulcanizing systems and/or its donors, in general, can be classified as in the following table:

enxofre (S): sulphur (S)

acelerador (A): accelerator (A)

convencional: conventional

semi - eficiente: half effective

eficiente: effective

5 Conventional systems: give good flexion and wear resistance and optimum tearing resistance. The permanent compressive deformation (DPC) is poor.

Half effective systems: give optimum flexion and wear resistance, good heat resistance, medium permanent compressive deformation (DPC).

10 Effective systems: give low flexion and wear resistance. Excellent heat and permanent compressive deformation resistance (DPC).

 Other forms of intermolecular linkages, which should be mentioned are:

15 * "Vulcanization" by organic or inorganic peroxides with or without using co-agents;

 * Super accelerated electrons or diverse super accelerators are also possibly usable as a way of "vulcanizing" elastomers;

20 The compositions of the invention can also comprise pigments, accelerators, cure agents, fillers, plasticizers, flux agents, anti oxidants, anti ozonants, cure co-agents and so on, selected under those conventionally used in the rubber production technique;

25 The present invention will be illustrated, but not limited, by the following examples:

Reference example (1) - physical properties:

 In a double SCREW extrusion machine (L/D = 32; 40 mm) the following composition has been mixed:

30 COMPONENTSphr

 Kraton KX 224 ES¹ 60

 Kraton KD 4270 BS² 40

 syndiotactic polybutadiene²⁵

 HI EDN 492 polystyrene^{12,5}

35 Shellflex 451³ 15

Irganox 1010⁴0,2

¹ thermoplastic elastomer

² thermoplastic elastomer

³ plasticizing oil

5 ⁴ antioxidant

After blending in the extrusion machine, the material was injected at 190 °C (Battenfelf extrusion machine BA 250/050 CDC).

10 Results of the reference composition analysis are given in the table below.

PROPERTIESRESULTS

Abrasion DIN mm³236

Shore hardness A - 15 seconds65.7

Density, g/cm³0.95

15 Flow index g/10 min (5 kg - 190 °C)3.65

Module @ 300%, Mpa3.65

Elongation in breaking, %435.0

Tension resistance, Mpa4.99

"dull - look" effect (opacity)standard

20 Example 01 of the Invention:

The following composition was mixed in the same double screw extrusion machine (L/D = 32; 40 mm):

COMPONENTSphr

Kraton KX 224 ES 60

25 Kraton KD 4270 BS40

acrylonitrile -butadiene copolymer 25

HI EDN 492 polystyrene12.5

Shellflex 45115

Irganox 10100.2

30 After compounding in the extrusion machine, the material was injected at 190 °C (Battenfelf extrusion machine BA 250/050 CDC).

Results of the reference composition analysis are given in the Table below.

35 PROPERTIESRESULTS

Abrasion DIN mm³258

Shore hardness A - 15 seconds61.5

Density, g/cm³0.96

Flow index g/10 min (5 kg - 190 °C)18.60

5 Module @ 300%, Mpa3.62

Elongation in breaking, %453,9

Tension resistance, Mpa4,43

"dull - look" effect (opacity)standard

Example 02 of the Invention (physical properties):

10 The following composition was mixed in the same
double screw extrusion machine (L/D = 32; 40 mm):

COMPONENTS phr

Kraton KX 224 ES 60

Kraton KD 4270 BS 40

15 butadiene-acrylonitrile-crossling

agent terpolymer 25

HI EDN 492 polystyrene 12.5

Shellflex 451 15

Irganox 10100,2

20 After compounding in the extrusion machine, the
material was injected at 190 °C (Battenfelf extrusion
machine BA 250/050 CDC).

Results of the reference composition analysis are
given in the Table below.

25 PROPERTIESRESULTS

Abrasion DIN mm³234

Shore hardness A - 15 seconds64,2

Density, g/cm³0,96

Flow index g/10 min (5 kg-190°C)18,80

30 Module @ 300%, Mpa3,72

Elongation in breaking, %432,2

Tension resistance, Mpa4,44

"dull - look" effect (opacity)above standard

Example 03 of the Invention (physical properties):

The following composition was mixed in the same double screw extrusion machine (L/D = 32; 40 mm):

COMPONENTS phr

5 Kraton KX 224 ES 60
Kraton KD 4270 BS 40
butadiene-acrylonitrile-crosslinking
agent terpolymer 35
HI EDN 492 polystyrene 12.5
Shellflex 451 15
10 Irganox 1010 0.2

After compounding in the extrusion machine, the material was injected at 190 °C (Battenfelf extrusion machine BA 250/050 CDC).

15 Results of the reference composition analysis are given in the Table below.

PROPERTIES RESULTS

Abrasion DIN mm³ 260
Shore hardness A - 15 seconds 65.2
Density, g/cm³ 0.96
20 Flow index g/10 min (5 kg - 190 °C) 19.50
Module @ 300%, Mpa 3.12
Elongation in breaking, % 567.8
Tension resistance, Mpa 3.96
"dull - look" effect (opacity) above standard

25 The composites blended (mixed) with NBR copolymers or terpolymers, in combination with thermoplastic rubbers have a variety of applications, such as:

Shoe Industry

- 30 shoes)
1. solid soles for casual shoe (tennis, walking
 2. expanded soles for casual shoe
 3. soles for safety boots
 4. heels
 5. boot heels
 - 35 6. welts

7. insoles, as an additive for ethylene-vinylacetate (EVA) and the like

8. total or partial PVC substitution for injected boots for use in cold storage rooms

5 Automotive Industry

1. extruded and expanded profiles for door sealing

2. sealings

3. dust covers for homo kinetic junctions (coifs)

10 4. retainer for motor carters exposed to temperature and lubricant oil action

5. hoses for hydraulic fluids (wheel and/or brakes)

6. total substitution of the windshield wiper

7. damper seats

15 Toys and Sports Industry

1. cars

2. dolls made up by rotormoulding or injection

3. balls

4. pins

20 5. fitting parts

6. holding articles

7. injected tires for two wheel vehicles

8. paddles

9. snorkels

25 10. belts, air ducts and diving masks

11. watch belts

Printing Industry

1. special drawing erasers

Hygienic and Personal Cleaning Industry

30 1. toothbrush handle (soft touch)

2. hairbrushes

3. combs

4. hair strips/clamps

5. raincoats

35 6. glass frames

7. buckets
8. receptacles
9. ice forms
10. glasses

5 Adhesive Industry

1. multi-utilisation adhesives for polar and non polar surfaces

Paint Industry / Building

1. underwater surface coverings
- 10 2. solvent based automotive paints stone resistant
3. airport and bridge paving expansion joints
4. water proof covers mixed with asphalt

Electricity Industry

1. low voltage wire and cable coverings
- 15 The blends (mixtures), of the invention, present special properties and can be used in all above mentioned applications. Such applications are mentioned herein for as an example, illustrative purposes only.

 The thermoplastic NBR rubber composite (TR) can be
20 produced in many ways. The most usual is by mixing NBR powder with TR powder in speedy mixers, "Henschel" type or helical mixers, concrete mixers or also by simple drumming, which consists of physically mixing the two components in any type of drum, container, bucket, etc. After this step,
25 the mixture can be added to any kind of extrusion machine, mono or double screw extrusion machine, co-rotating or counter-rotating, extruded, then pelletized for subsequent processing in thermoplastic transforming industry equipment. The final blended form, in powder, pellets, grumps, mats or
30 wires is not obstructive nor restrictive for their posterior use and do not influence the final properties claimed in the artefact produced by them.

 The utilisation of NBR as a dulling or opacity agent, besides presenting good dullness results, increase

the solvent resistance of the final blend, as described in the examples below.

Reference Example 02 (chemical resistance of the blend)

5 The following composition was mixed in the same double screw extrusion machine (L/D = 32; 40 mm):

COMPONENTS phr

Kraton KX 224 ES 60

Kraton KD 4270 BS 40

10 syndiotactic polybutadiene 25

HI EDN 492 polystyrene 12,5

Shellflex 451 15

Irganox 1010 0,2

15 After compounding in the extrusion machine, the material was injected at 190 °C (Battenfelf extrusion machine BA 250/050 CDC).

Results of the reference composition example 02 analysis are given in the Table below.

PROPERTIES RESULTS

20 swelling after ageing in hexane;

70 @ room temperature %+ 36.5

Swelling after ageing in cooking oil;

70h @ room temperature %+ 16.6

Swelling after ageing in fuel 2

25 70h @ room temperature %+ 21.6

Swelling after ageing in fuel 3

70h @ room temperature %+ 49,4

"dull look" effect (opacity) standard

30 Example 04 of the Invention (chemical resistance of the blend)

The following composition was mixed in the same double screw extrusion machine (L/D = 32; 40 mm):

COMPONENTS phr

Kraton KX 224 ES 60

35 Kraton KD 4270 BS 40

butadiene-acrylonitrile-
crosslinking agent 25
HI EDN 492 polystyrene 12,5
Shellflex 451 15

5 Irganox 1010 0.2

After compounding in the extrusion machine, the material was injected at 190 °C (Battenfelf extrusion machine BA 250/050 CDC).

10 Results of the reference composition example 04 analysis are given in Table below.

PROPERTIES RESULTS

swelling after ageing in hexane;

70 @ room temperature % + 16.7

Swelling after ageing in cooking oil;

15 70h @ room temperature % + 2.3

Swelling after ageing in fuel 2

70h @ room temperature % + 11.4

Swelling after ageing in fuel 3

70h @ room temperature % + 21.7

20 "dull look" effect (opacity) standard

A comparison between the reference Example 02 and Example 04 of the invention clearly denotes the blend advantages, with NBR referring to the blends of the prior art, in the properties of resistance to several solvents.

25 Another way of mixing the two compounds is by feeding them into normally used mixers employed in normally used mixers, used in the thermoset rubber-transforming industry, such as inner mixers "Banbury" or "Kneader" type, utilising Banburry or Sigma, Roller or Cam rotors or any
30 other normally used rotor. Similarly, open cylinder mixers can also be successfully used to process the blend (mixture) of the invention. With the ready mixture, in any kind of mixing equipment largely used in the thermoset rubber industry, it can be processed afterwards in any kind of mono
35 or double screw, co-rotational or counter-rotational

extrusion machine, extruded and pelletized for subsequent processing in thermoplastics transforming industry equipment. With this same mixture, processed in thermoplastic rubber industry mixing equipment, in case
5 adhesives and conventional additives components of said industry field are added, such as sulphur, vulcanization agents, primary accelerators, secondary accelerators, plasticizers, flow adjuvants, activators, fillers, antiozonants, antioxidants, etc., a vulcanizable composition
10 can be obtained in any kind of equipment, such as simple presses or transferring presses, injection machines, autoclaves, vulcanizing tunnels, etc., which render superior final properties to the same products when employing the prior art techniques, notably in their solvent and abrasion
15 resistance properties.

Reference Example 03 (vulcanized blend (mixture))

In a LUXOR MBL 150 cylinder mixer the below mentioned components are added, in the following sequence:

	COMPONENTS	phr
20	Kraton KX 224 ES	60
	Kraton KD 4270 BS	40
	syndiotactic polybutadiene	25
	HI EDN 492 polystyrene	12.5
	Shellflex 451	15
25	Ultrasil VN3 (silica)	25
	Irganox 1010	0.2
	Stearylene	1,0
	Zinc oxide	3.0
	Sulphur	1.4
30	MBTS	0.16
	Santocure MOR	1.35

After compounding during 15 minutes @ 60 °C, test samples were vulcanized in specific moulds in a press, after the rheometric curve @ 160 °.

Results of the reference composition example 05 analysis are given in Table below.

PROPERTIES RESULTS

Abrasion DIN mm³ 231.0

5 Shore hardness A - 15 seconds 85,0

Swelling in oil ASTM 1: 72h+42,1

Room temperature %

Elongation in breaking, % 385.0

"dull - look" effect (opacity) standard

10 Reference Example 05 (vulcanized blend (mixture))

In a LUXOR MBL 150 cylinder mixer the below mentioned components are added, in the following sequence:

COMPONENTS phr

Kraton KX 224 ES 60

15 Kraton KD 4270 BS 40

butadiene-acrylonitrile-

crosslinking agent terpolymer 25

HI EDN 492 polystyrene 12,5

Shellflex 451 15

20 Ultrasil VN3 (silica) 25

Irganox 1010 0.2

Stearyne 1.0

Zinc oxide 3.0

Sulphur 1.4

25 MBTS 0.16

Santocure MOR 1.35

After compounding during 15 minutes @ 60 °C, test samples were vulcanized in specific moulds in a press, after the rheometric curve @ 160 °.

30 Results of the reference composition example 05 analysis are given in Table below

PROPERTIES RESULTS

Abrasion DIN mm³ 197,0

Shore hardness A - 15 seconds 81,0

35 Swelling in oil ASTM 1: 72h+18,1

Room temperature %

Elongation in breaking, %430.0

"dull - look" effect (opacity) like standard

5 Dulling or opacity effect was maintained, with a lesser abraded volume and lesser swelling percentage, which denotes a blend with better properties than that of the prior art.

10 The composition of the invention presents a superior non-polar solvent resistance, compared with those compositions in which a polymer of the prior art is used.

Accordingly the composition of the invention is particularly appropriate for making parts, such as hoses, gaskets, sealings, coifs profiles, etc., in which a high organic solvent resistance is required.

15 Although the invention has been described with reference to specific embodiments contemplated herein, it has to be understood that many modifications and alterations apparent to those skilled in the art, to which this invention belongs, can be performed, which fall within the
20 scope of the invention as defined in the appended claims.

CLAIMS

1. Polymeric composition **CHARACTERIZED** in that it comprehends 5 to 95 parts of butadiene-acrylonitrile copolymer (NBR) or butadiene-acrylonitrile (NBR)-
5 crosslinking monomer terpolymer with 95 to 5 parts of thermoplastic elastomer per 100 parts of the composition;
wherein the crosslinking monomer is selected from those having a functionality ≥ 3 and said thermoplastic elastomers are selected from monoblocked, diblocked,
10 triblocked, radial or linear.
2. Composition of claim 1, **CHARACTERIZED** in that it comprised more preferably from 5 to 95 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile crosslinking monomer terpolymer per 100 parts of the said
15 thermoplastic elastomer composition.
3. Composition of claim 2, **CHARACTERIZED** in that it comprises more preferably from 5 to 80 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer terpolymer per 100 parts
20 of said thermoplastic elastomer composition.
4. Composition of claim 3, **CHARACTERIZED** in that it comprises more preferably from 5 to 70 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer terpolymer per 100 parts
25 of said thermoplastic elastomer composition.
5. Composition of claim 1, **CHARACTERIZED** in that the crosslinking monomer preferably comprises divinyl benzene, trimethylol propane trimethacrylate, ethylene glycol dimethacrylate and triallyl isocyanate.
- 30 6. Composition of claim 1, **CHARACTERIZED** in that said acrylonitrile monomer varies from 1 to 60% by weight, based on the weight of butadiene and acrylonitrile monomers of the NBR.
7. Composition of claim 6, **CHARACTERIZED** in that,
35 preferably, said acrylonitrile monomer varies between 15 to

45% by weight, based on the weight of butadiene and acrylonitrile monomers of the NBR.

8. Composition of claim 1, **CHARACTERIZED** in that said crosslinking monomer is present in an amount ranging from 0 to 20% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

9. Composition of claim 8, **CHARACTERIZED** in that said crosslinking monomer is preferably present in an amount ranging from 0 to 10% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

10. Composition of claim 9, **CHARACTERIZED** in that said crosslinking monomer is present in an amount ranging preferably from 0 to 5% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

11. Composition of claim 1, **CHARACTERIZED** in that said thermoplastic elastomer is selected from styrene - butadiene - styrene, (SBS), styrene - isoprene - butadiene - styrene (SIBS), styrene - isoprene-butadiene-styrene (SSBS), styrene- isoprene -styrene (SIS).

12. Composition of any of claims 1 to 11, **CHARACTERIZED** in that the final article produced by said composition presents a dull-look (opacity).

13. Composition of any of claims 1 to 12, **CHARACTERIZED** in that it can further comprises pigments, plasticizers, flow agent, antioxidants and antiozonants.

14. Composition of any of claims 1 to 13, **CHARACTERIZED** in that it has a superior non-polar solvent resistance.

15. Polymeric vulcanizable composition **CHARACTERIZED** in that it comprises 5 to 95 parts of butadiene-acrylonitrile copolymer (NBR) or butadiene-acrylonitrile(NBR)-crosslinking monomer terpolymer with 95 to 5 parts for thermoplastic elastomer per 100 parts of said composition and an effective amount of vulcanizing system;

wherein said crosslinking monomer is selected from those having a functionality ≥ 3 and said thermoplastic elastomers are selected from monoblocked, diblocked, triblocked, radial or linear of vulcanising system.

5 16. Composition of claim 15, **CHARACTERIZED** in that it comprises more preferably from 5 to 95 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer terpolymer per 100 parts of said thermoplastic elastomer composition.

10 17. Composition of claim 16, **CHARACTERIZED** in that it comprises more preferably from 5 to 80 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer terpolymer per 100 parts of said thermoplastic elastomer composition.

15 18. Composition of claim 17, **CHARACTERIZED** in that it comprises more preferably from 5 to 70 parts of butadiene-acrylonitrile copolymer or butadiene-acrylonitrile-crosslinking monomer terpolymer per 100 parts of said thermoplastic elastomer composition.

20 19. Composition of claim 15, **CHARACTERIZED** in that said crosslinking monomer preferably comprises divinyl benzene, trimethylol propane trimethacrylate, ethylene glycol dimethacrylate and triallyl isocyanate.

25 20. Composition of claim 15, **CHARACTERIZED** in that said acrylonitrile monomer varies from 1 to 60% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

30 21. Composition of claim 20, **CHARACTERIZED** in that, preferably, said acrylonitrile monomer varies from 15 to 45% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

35 22. Composition of claim 15, **CHARACTERIZED** in that said crosslinking monomer is present in an amount ranging from 0 to 20% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

23. Composition of claim 22, **CHARACTERIZED** in that said crosslinking monomer is preferably present in an amount ranging from 0 to 10% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

5 24. Composition of claim 23, **CHARACTERIZED** in that the crosslinking monomer is preferably present in an amount ranging from 0 to 5% by weight based on the weight of butadiene and acrylonitrile monomers of the NBR.

10 25. Composition of claim 15, **CHARACTERIZED** in that said thermoplastic elastomer is selected from styrene-butadiene-styrene, (SBS), styrene-isoprene-butadiene-styrene (SIBS), styrene-isoprene-butadiene-styrene (SSBS), styrene-isoprene-styrene (SIS).

15 26. Composition of any of claims 15 to 25, **CHARACTERIZED** in that the final article produced by the composition presents a dull-look (opacity).

27. Composition of any of claims 15 to 26, **CHARACTERIZED** in that it can further comprised pigments, plasticizers, flow agent, antioxidants and antiozonants.

20 28. Composition of any of claims 15 to 27, **CHARACTERIZED** in that it has a superior non-polar solvent resistance.

25 29. Composition of claim 15, **CHARACTERIZED** in that the vulcanization system is selected from sulphur and/or its donor, primary accelerators, secondary accelerators, tertiary accelerators, peroxides, silanes, crosslinking agents and mixtures thereof and also electron accelerators.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR00/00073

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : CO8L 9/02 US CL : 525/99 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 525/99 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) none				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 5,055,519A (ONO et al.)08 October 1991, Table 1.	1-12, 15-26, 29		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.				
<table border="0"> <tr> <td style="vertical-align: top;"> <p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="vertical-align: top;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>*Z* document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>*Z* document member of the same patent family</p>
<p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>*Z* document member of the same patent family</p>			
Date of the actual completion of the international search 24 OCTOBER 2000		Date of mailing of the international search report 08 DEC 2000		
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